



CERTIFIED EXPERIMENT REPORT

Date: August 4, 2006

5 Experiment Duration: July 18 to 28, 2006

Locations: 1. Sample Fabrication

1) Labo Plastomill mixing

FUKOKU CO., LTD., Research Center

10 2) Roll mixing

NISSIN KOGYO CO., LTD., Nagano Development Center

2. Sample Fabrication

Press molding

NISSIN KOGYO CO., LTD., Nagano Development Center

15 3. Evaluation (tension experiments)

NISSIN KOGYO CO., LTD., Nagano Development Center

4. Evaluation (measurement using pulsed NMR technique;
observation by electron microscope)

NISSIN KOGYO CO., LTD., Nagano Development Center,

20 AREC Research Group

Reported by: Toru Noguchi

NISSIN KOGYO CO., LTD.

840, Ohaza Kokubu, Ueda-shi, Nagano 386-8505, Japan

25

Resume of Toru Noguchi:

Work Experience

-Staff developer and researcher of elastomer and metal composite material, NISSIN KOGYO CO., LTD., July 2002 – current

-Staff developer and researcher of mainly elastomer, MITSUBOSHI BELTING LTD., April 1986 – 2001

5

Education

-Completed doctoral course in materials engineering, Graduate School of Science and Technology, Kobe University, Hyogo Japan, March 1986

-BS Metal engineering, Department of Engineering, Tohoku

10

University, Miyagi Japan, March 1977

1. Objective of experiment

(1) To clarify the technical difference between the present invention and the composite material of the cited reference.

15

(2) To demonstrate that carbon nanofibers are not uniformly dispersed in the composite material of the cited reference.

2. Experimental method

(1) Test 1

Example 1 described in the cited reference 1 (Japanese Patent Application

20

No. 2003-551203 (WO03/050181)) was double-checked. The first spin-spin relaxation time (T_{2n}), the second spin-spin relaxation time (T_{2nn}), and the fraction (f_{nn}) of components having the second spin-spin relaxation time of an uncrosslinked sample were measured at 150°C by the Hahn-echo method using the pulsed NMR technique in the same manner as in Example 1 described in the Specification of the present application to evaluate the dispersion state of the carbon nanofibers.

25

(a) Preparation of uncrosslinked sample

1) NR (100 parts by weight (phr)) was placed in a Labo Plastomill (model: B600)

manufactured by Toyo Seiki Seisaku-Sho, Ltd., and masticated at 70°C and 50 rpm for three minutes. The temperature of the apparatus at the end of mastication was 86°C.

2) Additives shown in Table 1 excluding the vulcanization accelerator and sulfur were added to the NR, and the components were mixed at 70°C and 30 rpm for five minutes. The temperature of the apparatus at the end of mixing was 100°C. As the carbon nanofibers, multi-wall carbon nanotubes with an average diameter of about 13 nm manufactured by Iljin Nanotech Co., Ltd. were used.

3) The mixture obtained in 2) was removed, cooled, and weighed. After adding the remaining vulcanization accelerator and sulfur, the components were again mixed at 50°C and 30 rpm for three minutes to obtain an uncrosslinked sample. The temperature of the apparatus at the time of removal was 86°C.

Note: In the cited reference 1, a Brabender is used to mix the vulcanization accelerator and sulfur. On the other hand, the Labo Plastomill was used in this experiment. The Brabender is a mixer manufactured by an overseas manufacturer (Brabender GmbH & Co. KG) and is similar to the Labo Plastomill manufactured by Toyo Seiki Seisaku-Sho, Ltd. These apparatuses are relatively small mixers generally called intermixers^(*) with a mixing amount of about 200 g to 1 kg. It is a general practice to determine optimum conditions using an intermixer before mass production using a large Banbury mixer^(*) (mixing amount: 50 to 500 kg) or a pressure kneader^(*) (mixing amount: 10 to 200 kg). Since the shearing force applied per unit amount of elastomer using the small intermixer is greater than that of a large mixer, fillers can be easily dispersed using the intermixer in comparison with the large mixer. Therefore, fillers which are not uniformly dispersed using the intermixer generally cannot be uniformly dispersed using the large mixer.

(*) Reference: Basic Rubber Technology (new edition) (edited by The Society of

Rubber Industry, Japan), published on April 30, 1999, p. 239 and 240

(b) Measurement using pulsed NMR technique

Each uncrosslinked sample was subjected to measurement by the Hahn-echo
5 method using the pulsed NMR technique. The measurement was conducted using a
“JMN-MU25” manufactured by JEOL, Ltd. The measurement was conducted under
conditions of an observing nucleus of ^1H , a resonance frequency of 25 MHz, and a
90-degree pulse width of 2 microseconds. A decay curve was determined while
changing P_i in the pulse sequence ($90^\circ\text{x-Pi-}180^\circ\text{x}$) of the Hahn-echo method. The
10 sample was inserted into a sample tube within an appropriate magnetic field range.
The measurement temperature was 150°C . The first and second spin-spin
relaxation times (T_{2n} and T_{2nn}) and the fraction (f_{nn}) of components having the
second spin-spin relaxation time of the uncrosslinked sample were determined by
this measurement. The measurement results are shown in Table 1.

15 (c) Electron microscope observation

The uncrosslinked sample prepared in (a) was rolled to a thickness of 1.2 mm
using an open roll to obtain a sheet for crosslinking. The sheet was press-formed at
 175°C for 10 minutes to obtain a crosslinked sheet with a thickness of 1 mm. The
20 crosslinked sheet was subjected to a tensile test, and the tensile fracture surface was
observed using an electron microscope. Fig. 1 shows the electron micrograph. Since
the sample of the test 1 contained a large amount of carbon black and a small
amount of carbon nanofibers, it was difficult to identify carbon nanofiber aggregates
by checking with eyes.

25 (2) Test 2

A sample was obtained in the same manner as in the test 1 (a) except for

changing the mixing ratio of Example 1 of the cited reference 1 as shown in Table 1, and the dispersion state of the carbon nanofibers was evaluated in the same manner as in the test 1 (b). As shown in Table 1, since a small amount of carbon nanofibers and a large amount of additives other than the carbon nanofibers were mixed in the test 1, it was difficult to observe the aggregation state of the carbon nanofibers. In the test 2, the amount of carbon nanofibers was increased, and the additives other than the carbon nanofibers were not used. The measurement results are shown in Table 1. The sample of the test 1 was checked with eyes and using an electron microscope in the same manner as in the test 1 (c) to observe carbon nanofiber aggregates. Fig. 2 shows the electron micrograph.

(3) Test 3

The same components used in the test 2 were mixed using an open roll maintained at a specific temperature to obtain an uncrosslinked sample, and the dispersion state of the carbon nanofibers was evaluated in the same manner as in the test 1 (b). In the test 3, the effects of the temperature during mixture were investigated using an open-roll method in the same manner as in the examples of the present invention by setting the roll temperature at 60°C in test 3-1, at 90°C in test 3-2, and 120°C in test 3-3. The measurement results are shown in Table 1. The sample of the test 3 was checked with eyes and using an electron microscope in the same manner as in the test 1 (c) to observe carbon nanofiber aggregates. Figs. 3 to 5 show the electron micrographs.

TABLE 1

		Test 1	Test 2	Test 3		
Polymer material		NR	NR	3-1	3-2	3-3
Polar group		Double bond	Double bond	NR	NR	NR
Average molecular weight		3,000,000	3,000,000	Double bond	Double bond	Double bond
Raw material elastomer				3,000,000	3,000,000	3,000,000
	T2n (150°C)	5500	5500	5500	5500	5500
	(microsecond)					
	T2nn (150°C)	18000	18000	18000	18000	18000
Uncrosslinked form	(microsecond)					
	Fnn (150°C)	0.381	0.381	0.381	0.381	0.381
	Flow temperature (150°C)	40	40	40	40	40
	NR (phr)	100	100	100	100	100
Component	Carbon nanofiber (phr)	5	20	20	20	20
	HAF carbon black (phr)	50	0	0	0	0
	Alumina (phr)	0	0	0	0	0
	Aroma oil (phr)	10	0	0	0	0
	Hydrozincite (phr)	3	0	0	0	0
	Stearic acid (phr)	1	0	0	0	0
	Aging preventive (phr)	1	0	0	0	0
	Vulcanization accelerator (phr)	1	0	0	0	0
	Sulfur (phr)	1.5	0	0	0	0
Mixing method		Labo Plastomill		Roll mixing		
Roll mixing temperature (°C)				60	90	120
Composite material						
	T2n (150°C)	3880	3230	3280	3340	3310
	(microsecond)					
	T2nn (150°C)	6610	5380	8790	7940	7690
Uncrosslinked form	(microsecond)					
	Fnn (150°C)	0.448	0.541	0.215	0.223	0.271
	Flow temperature (150°C)	40	40	40	40	40

3. Experimental results

(1) The following items were confirmed from the experimental results shown in Table 1.

Regarding the measurement results of the samples of all the tests using the pulsed NMR technique, $T2n$ was longer than 3000 microseconds, and Fnn was greater than 0.2.

(2) The following items were confirmed from the electron micrographs shown in Figs. 1 to 5.

1) In the sample of the test 1, a small number of carbon nanofiber aggregates was observed in a large amount of carbon black.

2) In the samples of the tests 2 and 3, a number of large carbon nanofiber aggregates was observed. A number of large carbon nanofiber aggregates was also observed by checking with eyes.

4. Conclusion

The following items were confirmed from the tests 1, 2, and 3.

(1) The carbon nanofibers are uniformly dispersed in the carbon fiber composite material of the present invention, as shown in Table 1 and Figs. 4 to 6 of the Specification of the present application. On the other hand, the carbon nanofibers are not uniformly dispersed in the composite material of the cited reference 1, as is clear from the results of the tests 1 and 2. This is considered to be because the elastomer loses elasticity in the tests 1 and 2 due to an increase in temperature during mixing.

(2) When using the mixing method using the open-roll method as in the present invention, the carbon nanofibers cannot be uniformly dispersed in the elastomer

for the reason described in (1) when the mixing temperature is increased as in the test 3. Therefore, when using a general mixing method disclosed in the cited reference other than the cited reference 1, the carbon nanofibers cannot be uniformly dispersed since a large shearing force and the elasticity of the elastomer are not obtained.

Attachment:

Fig. 1: electron micrograph of the sample of the test 1

Fig. 2: electron micrograph of the sample of the test 2

Fig. 3: electron micrograph of the sample of the test 3-1

Fig. 4: electron micrograph of the sample of the test 3-2

Fig. 5: electron micrograph of the sample of the test 3-3

Basic Rubber Technology (new edition) (edited by The Society of Rubber Industry, Japan), published on April 30, 1999, pp. 238 to 241

FIG. 1 TEST 1

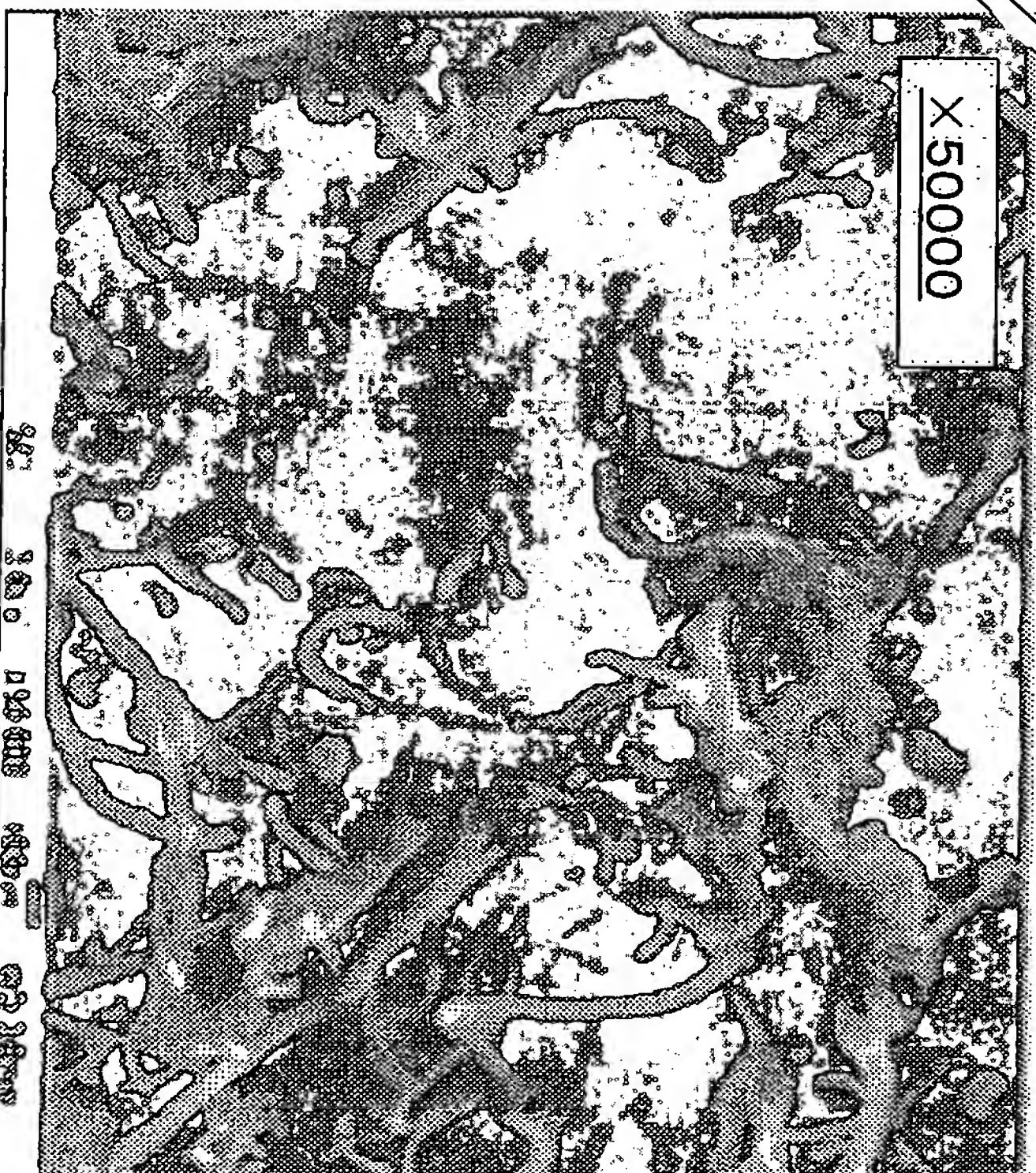
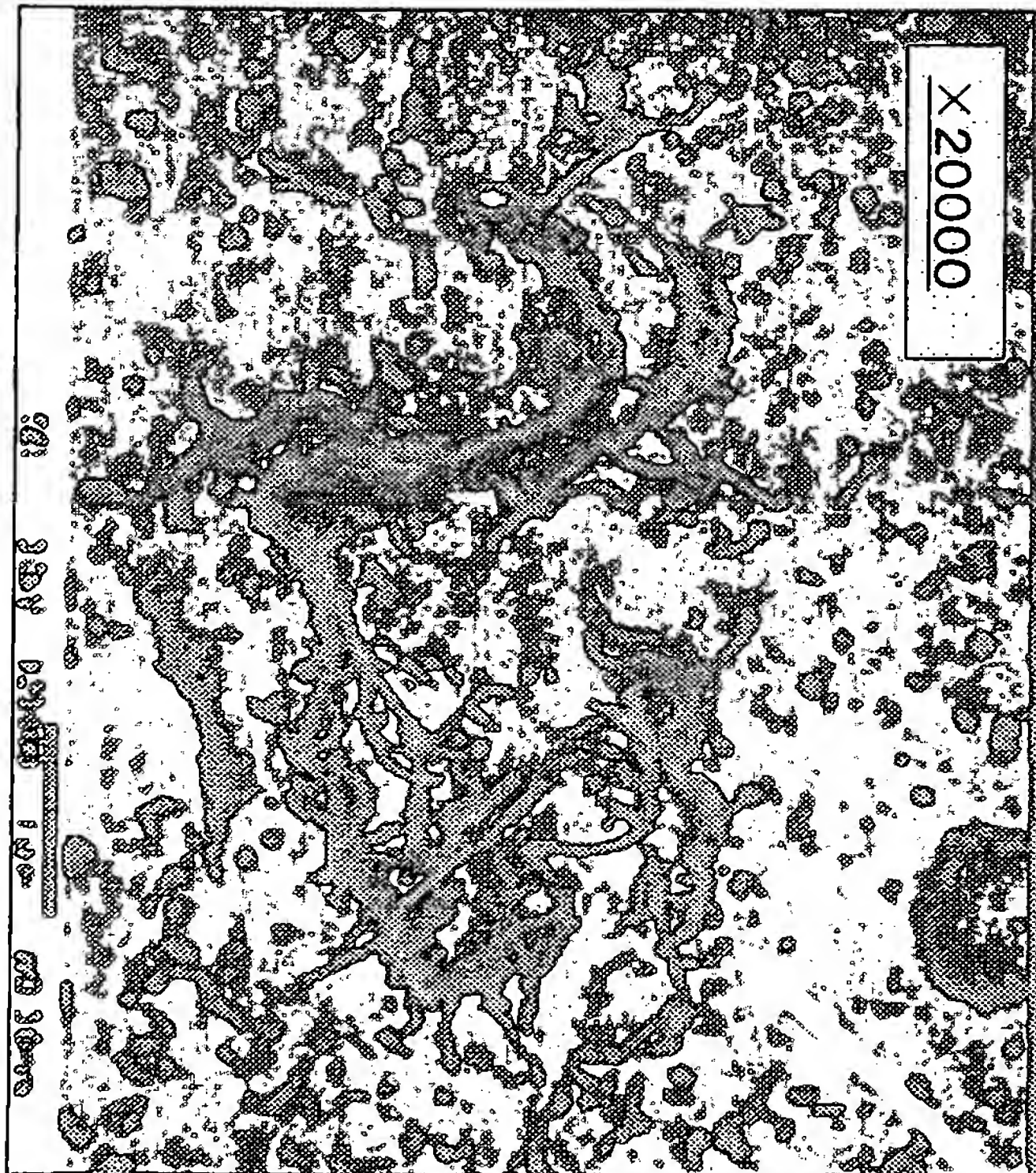
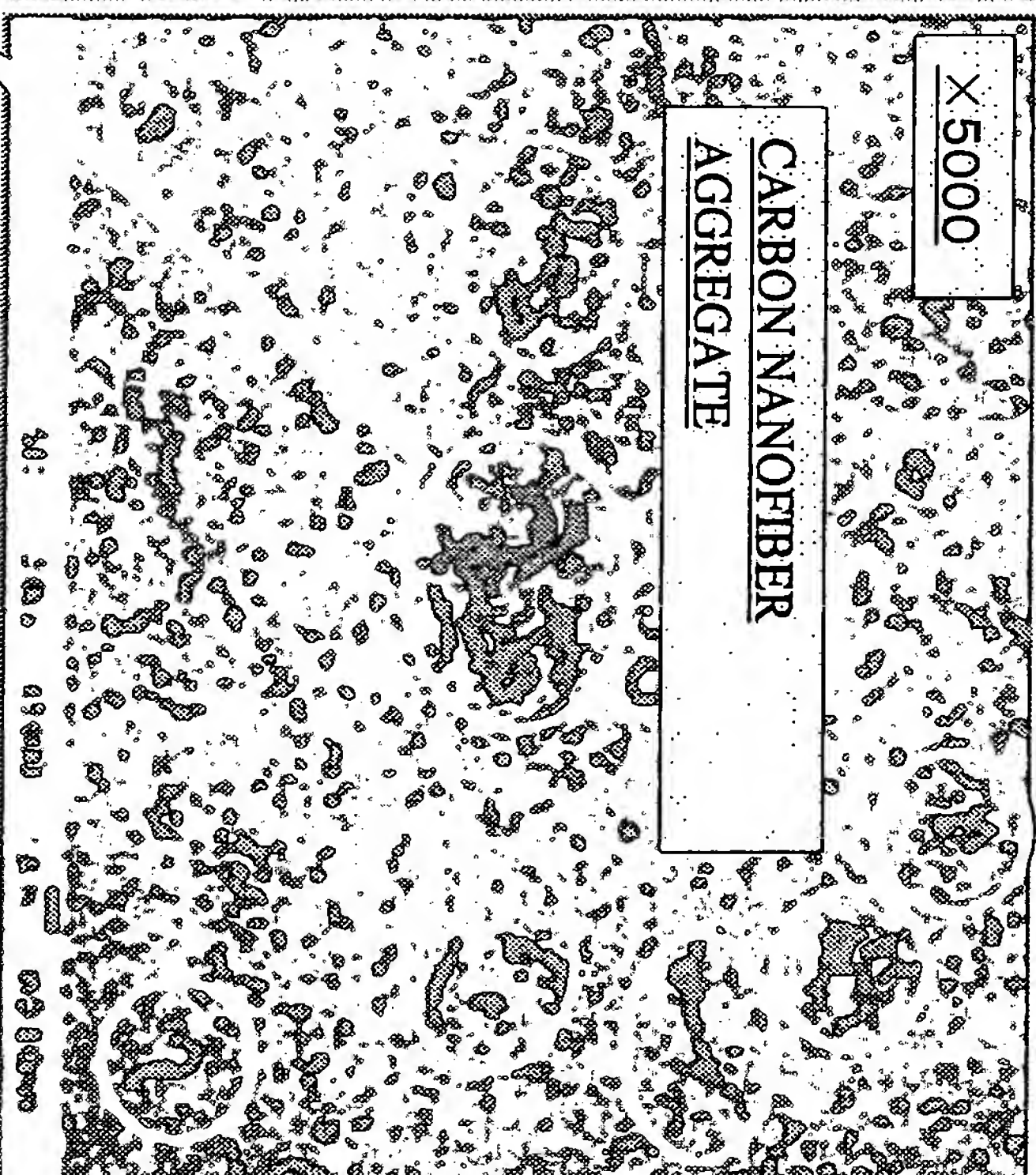
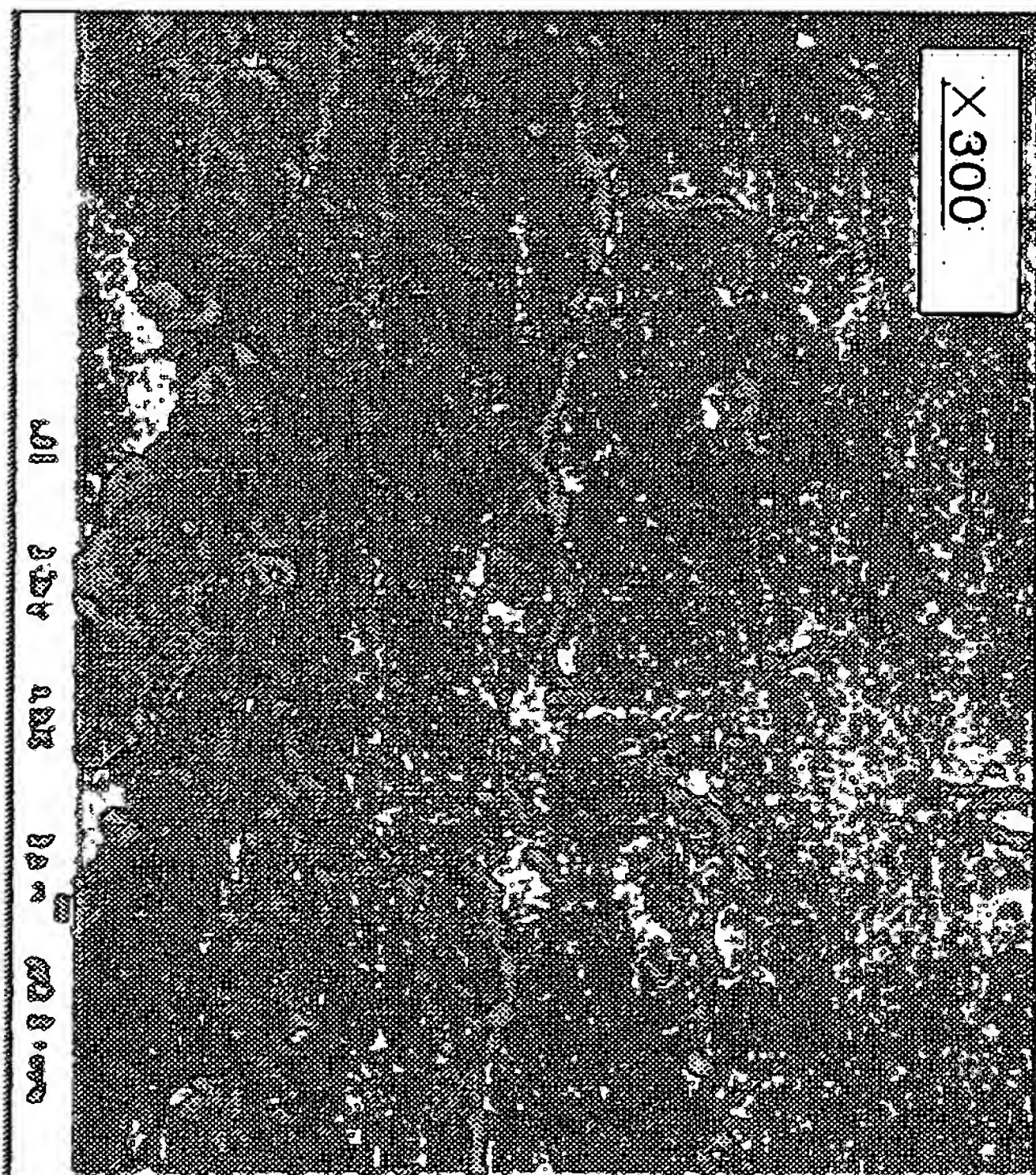


FIG. 2 TEST 2

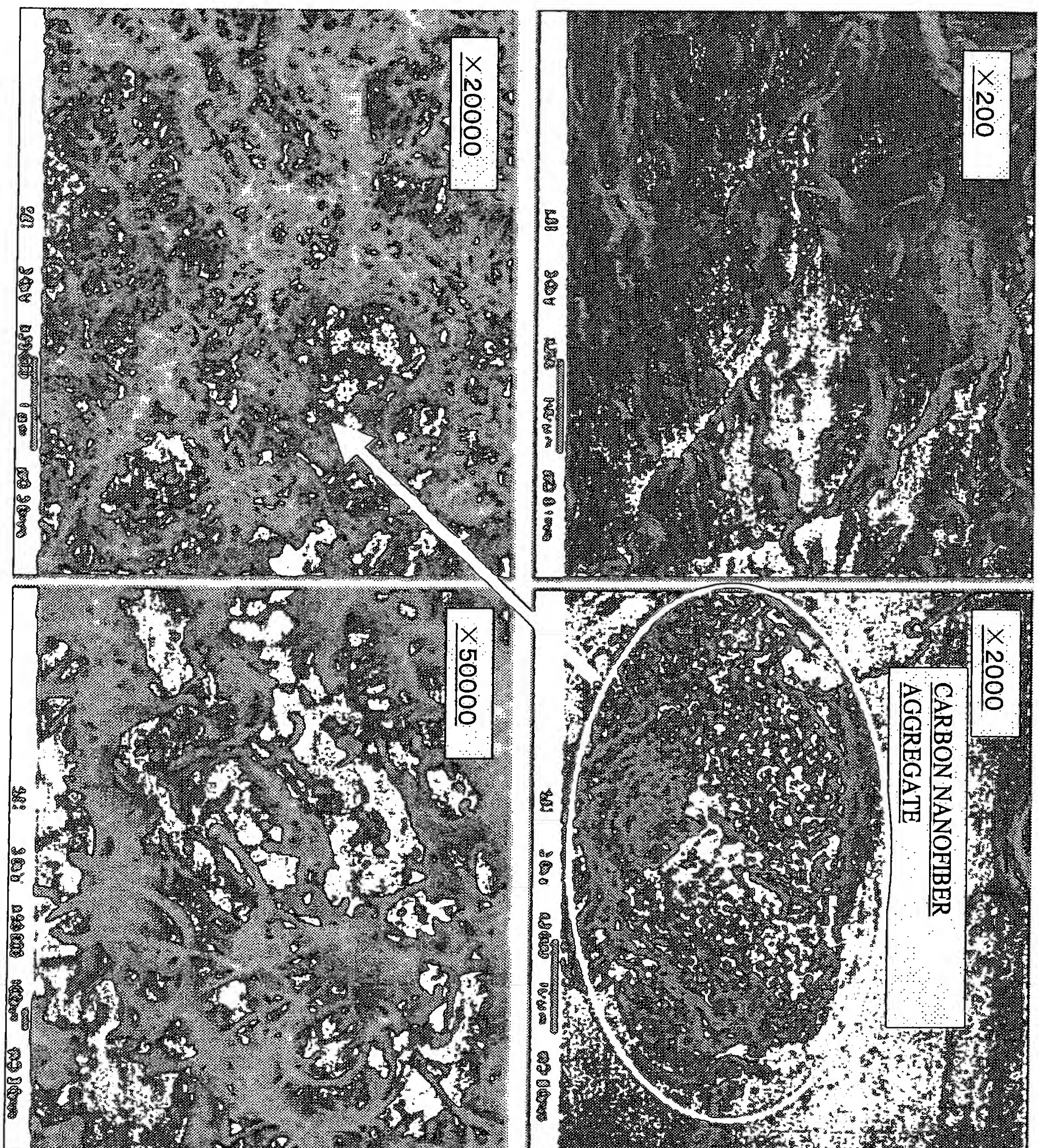


FIG.3 TEST 3-1: ROLL MIXING TEMPERATURE: 60°C

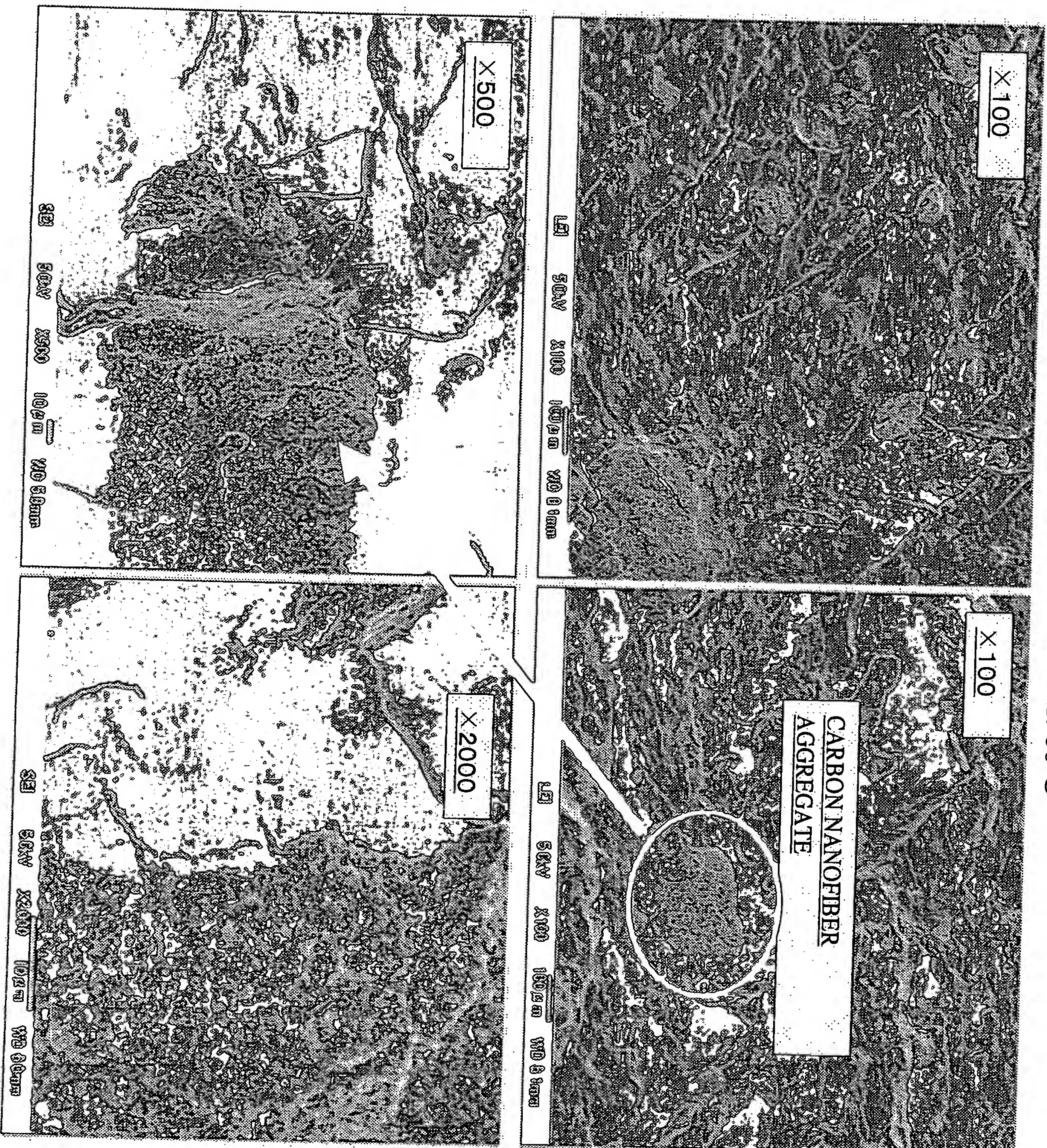


FIG.4 TEST 3-2: ROLL MIXING TEMPERATURE: 90°C

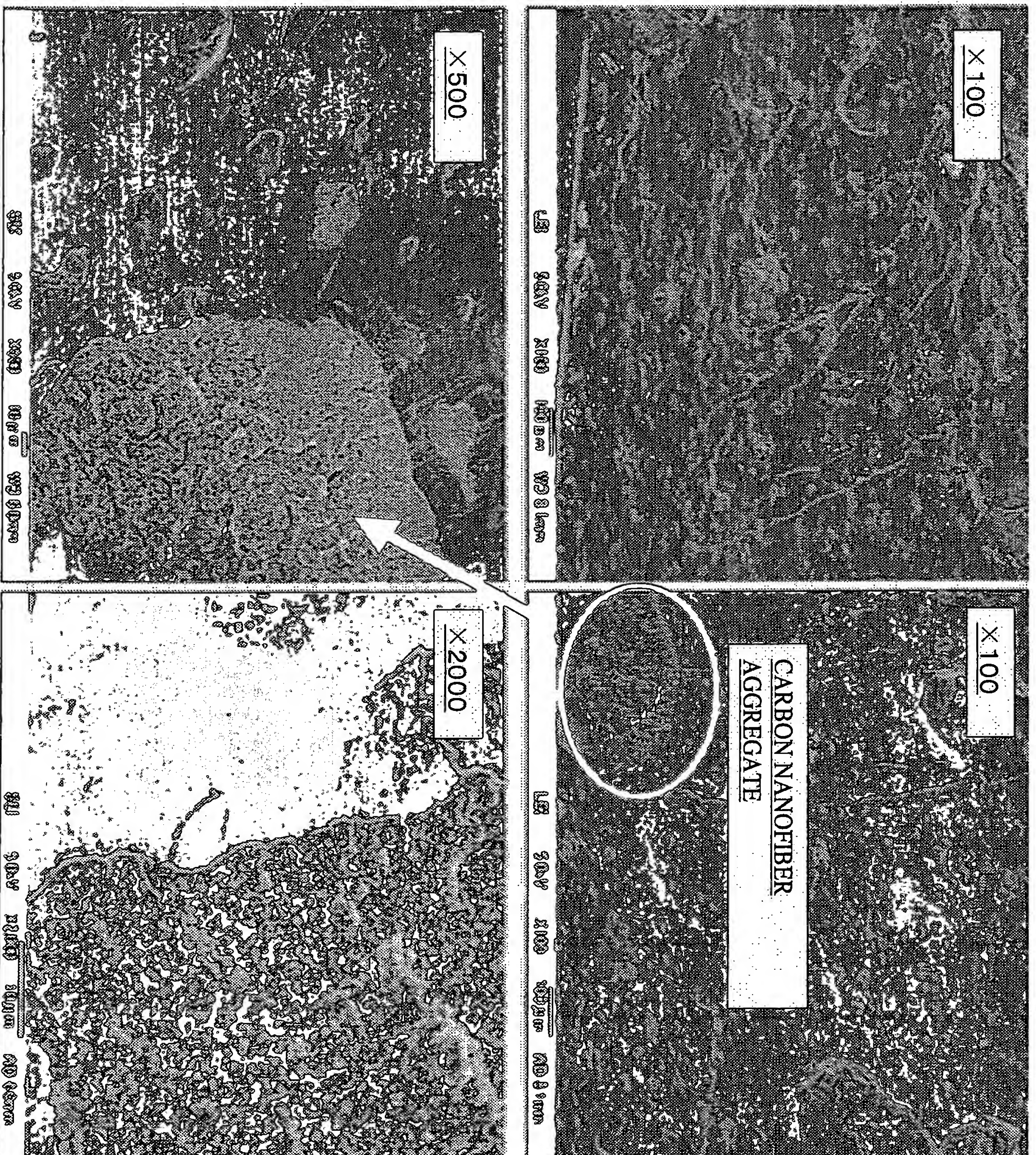


FIG.5 TEST 3-3: ROLL MIXING TEMPERATURE: 120°C

